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13. ABSTRACT (Maximum 200 words) This report reviews past battery studies using room-temperature chloroaluminate electrolytes, pointing out problems experienced. The report then summarizes attempts to circumvent these problems. A cell is described that uses a sodium anode, a copper (II) chloride cathode, and room-temperature chloroaluminate electrolyte buffered to the neutral composition. Cells give an open circuit voltage greater than 2.75 volts and discharge near 1 mA/cm ² at voltages greater than 2 volts for more than 20 hours. Cell failure is attributed to the formation of a nonconductive coating on the sodium electrode. Suggestions for future studies are presented. While the room-temperature chloroaluminates appear suitable for high-voltage, low-current batteries, their physical properties may limit their potential for high energy density batteries. <i>small Amperes per centimeters squared</i> <i>→ High Energy Density Batteries, Ionic Liquid</i>					
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PREFACE

This is the final report for FJSRL Work Unit 2303-F2-10. The purpose of this report then is to review where the battery research has been, the results to date, and the directions it should take. The report reviews past battery work in the MEIC-AlCl₃ molten salt electrolyte, both here and at other laboratories. It points out problems associated with these electrolytes and describes approaches taken to solve these problems. The report presents the latest results using sodium electrodes in buffered neutral chloroaluminate molten salt electrolytes at room temperature.

I would like to thank Mr. Jeffrey Boon and Dr. John Wilkes for their many helpful discussions. Special thanks to Ms. Maureen Parrish who made the many preparations of melt required for the cell studies. Finally, thanks to Mrs. Linda Pukajlo for formatting and printing the report.



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INTRODUCTION

Batteries with high gravimetric energy density (Wh/kg) require that voltage, current, and discharge time be maximized while minimizing mass. Molten salts such as LiCl-KCl are used as electrolytes to attain these characteristics. Molten salts are ionic liquids that facilitate current carrying capacity and minimize mass since no supporting electrolyte is needed. However, molten salts currently used in batteries are high-melting materials requiring high operating temperatures, greater than 350°C in the case of LiCl-KCl. High operating temperatures in batteries cause problems with corrosion, material compatibilities, and operating complexities.

Lower melting molten salts composed of mixtures of aluminum chloride and sodium chloride (m.p. 152°C) have been examined as electrolytes in high energy density batteries and found some success in thermal battery applications.^{1,2} Chloroaluminates containing a third component such as a second alkali metal salt have been used for electrolytes that are molten as low as 70°C.³

When aluminum chloride is mixed with an organic salt, melting points near room temperature are achieved. Some compositions of aluminum chloride and butylpyridinium chloride are liquid at or near room temperature. However, these melts are electrochemically limited by the reduction of the pyridinium cation.⁴

A search was conducted for an organic cation more resistant to reduction than pyridinium to make a room-temperature chloroaluminate melt with a wider electrochemical window. Candidate cations were screened using MNDO calculations.⁵ The results of this study indicated that dialkylimidazolium ions should work. Accordingly, an analogous series of dialkylimidazolium chloride salts were synthesized and found to form molten salts when mixed with aluminum chloride.⁶ One of the easiest to synthesize that also gave a melt with the best physical properties was 1-methyl-3-ethylimidazolium

chloride (MEIC). Melts made by mixing this salt with aluminum chloride give liquids at room temperature at all compositions between $N = 0.33$ and $N = 0.67$ where N is the mole fraction of aluminum chloride.

The chemistry of the organic chloroaluminate molten salts has been reviewed by Osteryoung.⁴ The chloroaluminate system can be described on the basis of the acid-base equilibrium:



The heptachloroaluminate ion is a strong Lewis acid and the chloride ion is its conjugate base. This equilibrium is analogous to the autoionization of water:



Compositions of $N < 0.50$ are said to be basic due to the dominance of the chloride ion. Compositions > 0.50 are acidic due to the heptachloroaluminate ion. At a composition of exactly $N = 0.50$, the only anion present in significant amounts is the tetrachloroaluminate ion and the melt is considered neutral. These composition regions have distinctly different chemical, physical, and electrochemical properties which have considerable ramifications when considered for use in batteries.

The anodic and cathodic limits, which are determined by the dominate ionic species present, determine the electrochemical window of an electrolyte. In basic organic chloroaluminate compositions, the dominate ions are the organic cation and tetrachloroaluminate anion. In MEIC- AlCl_3 melts, the cathodic limit is the reduction of MEI^+ at about -1.9 V relative to the $\text{Al}/\text{Al(III)}(N = 0.67)$ reference. The anodic limit is the oxidation of chloride at about $+1.0$ V. In acidic compositions, the cathodic limit is the

reduction of heptachloroaluminate to aluminum metal at -0.4 V and the evolution of chlorine from tetrachloroaluminate at $+2.5$ V. At exactly neutral composition the only ions present are the organic cation and the tetrachloroaluminate anion. The cathodic limit of the neutral melt is that of the basic melt, reduction of the organic cation, and the anodic limit is that of the acidic melt or the oxidation of tetrachloroaluminate to chlorine. Thus, the available electrochemical window in both basic and acidic MEIC melts is about 2.9 V whereas the window in neutral MEIC melts is 4.4 V. These values are about 0.9 V greater than in butylpyridinium melts. The voltammograms showing the melt limits for basic, acidic, and neutral MEIC—aluminum chloride molten salts are shown in Figure 1.

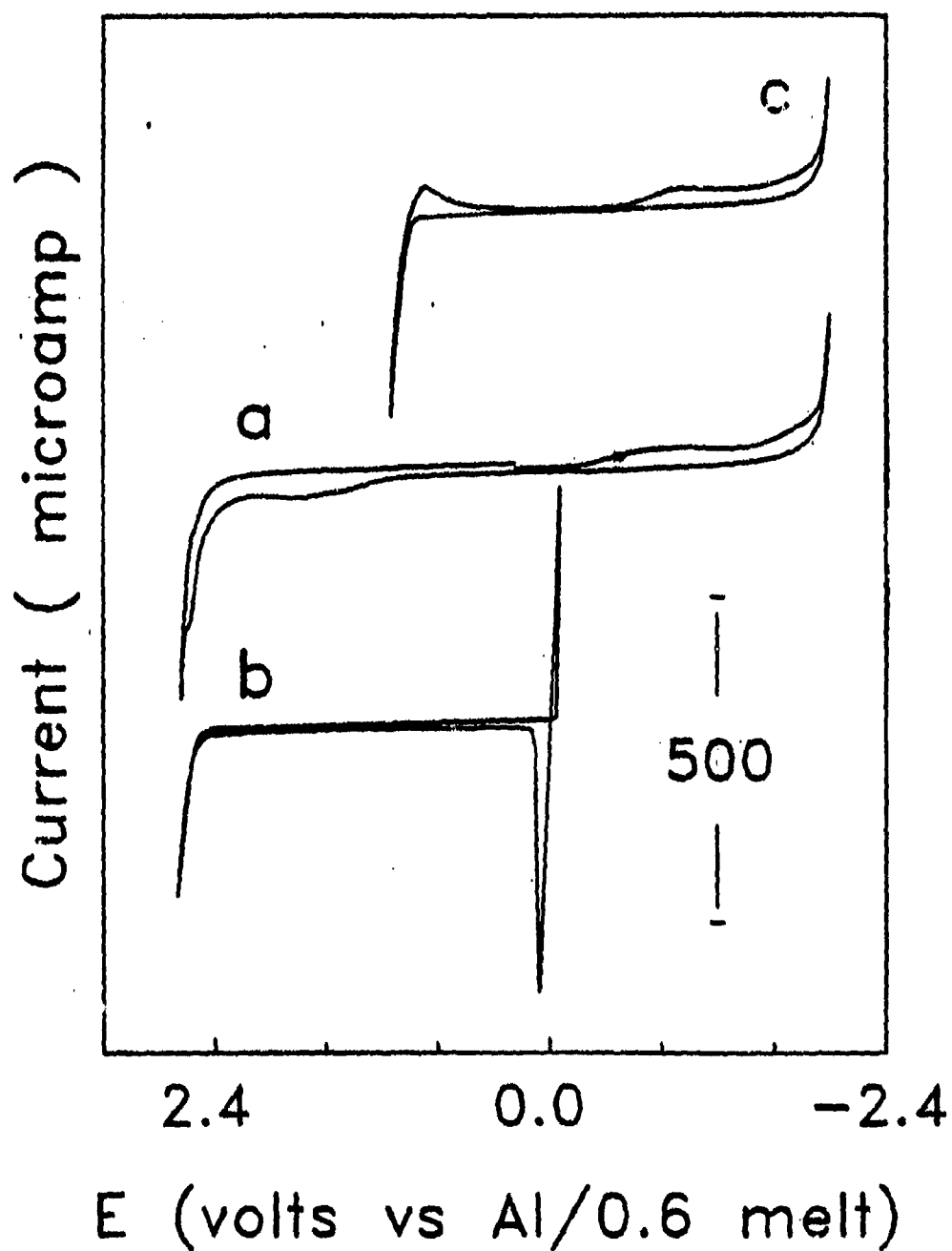


Figure 1. Electrochemical windows for aluminum chloride-1-methyl-3-ethylimidazolium chloride molten salts:
 a - neutral; b - acidic; and c - basic.

Densities, conductivities and viscosities of several dialkylimidazolium chloride-aluminum chloride melts were determined by Fannin *et. al.*⁷ Some representative data at various compositions are shown in Tables I and II.

N	$10^3 \kappa$ (mho/cm)
0.33	2.569
0.40	6.506
0.50	22.64
0.64	15.57
0.01 M KCl	1.408
0.1 M KCl	12.85

TABLE I. Specific conductivities at 25°C for MEIC-AlCl₃ melts at various compositions.⁷ Values for KCl solutions are shown for comparison.⁸

N	ν s/m ²
0.36	214
0.50	13.8
0.66	10.1
water	0.8903
glycerol	942

TABLE II. Kinematic viscosities at 25°C for MEIC-AlCl₃ melts at various compositions.⁷ Water and glycerol are given for comparison.⁹

PREVIOUS BATTERY STUDIES

The most favorable conductivities are in the neutral or acidic regions of melt composition. Also the magnitude of the changes are smaller across the acidic region than across the basic region. The neutral composition is the most favorable, but the exactly neutral composition could not be maintained during any cell reaction involving melt species. A survey of cations and electrode materials using cyclic voltammetry¹⁰ showed that the electrochemical properties of prospective electrode materials are complex in the acidic region of the melt, but relative simple in basic melts. In addition, voltages of prospective battery couples are higher in basic melts than in acidic melts. For these reasons most battery work has been in basic compositions. However, aluminum, a principal candidate as an anode, is not reversible in basic compositions but is reversible in acidic compositions.¹¹ Prospective cathode materials are quite soluble in both basic and acidic compositions and chlorine chlorinates the imidasolium cation.¹⁴

The first crude cell was constructed to demonstrate the use of these melts in a cell configuration.⁴ This first cell used basic MEIC-aluminum chloride as the electrolyte, an aluminum anode, and a pressed pellet cathode containing iron(III) chloride as the active material. The two electrodes were separated by a fine glass frit. The discharge of this cell demonstrated the feasibility of a battery made using these room-temperature molten salts. The cell was discharged at a current of 0.100 mA and an average voltage of 1.4 volts at 20°C. Benzene was added to the electrolyte to increase conductivity as well as to inhibit the solubility of the iron chloride.

Donahue made a preliminary study of electrochemical engineering requirements for batteries using room temperature chloroaluminate melts.¹² His study included the theoretical aspects of the chemistry and electrochemistry of possible battery couples in the melts. His report pointed out the many unknowns concerning the chemistry of these electrolytes and the disadvantages of their physical properties. Much of his discussion

pointed out the problems associated with the use of the Al/Cl₂ couple (energetically the most advantageous) in these melts.

Auborn studied the aluminum electrode in basic and acidic compositions. He showed that the aluminum is reversible with high efficiency in acidic compositions but irreversible in basic compositions.¹¹

Reynolds and Dymek demonstrated a number of configurations for primary and secondary cells.¹³ They examined the following configurations:

1. Al/AlCl₃-MEIC(N=0.37)//FeCl₃-MEIC(N=0.33)/W
2. Al/AlCl₃-MEIC(N=0.37)//WCl₆-MEIC(N=0.33)/W
3. Al/AlBr₃-MEIB(N=0.33)//Br₂/RVC,Pt
4. Zn/AlCl₃-MEIC(N=0.33)//AlCl₃-MEIC(N=0.60)/Al
5. Cd/AlCl₃-MEIC(N=0.33)//AlCl₃-MEIC(N=0.60)/Al

Cells 1, 2, 4, and 5 used ion exchange membranes as separators. Cell 3 had no "separator" except for the phase boundary between liquid bromine and the melt. Cells 1, 2, and 3 are primary cells since aluminum is not reversible in basic melts, while 4 and 5 are potentially secondary. The primary cells had open-circuit potentials of 1.75 to 2.19 V, whereas the secondary configurations gave open-circuit potentials of only 0.7 to 1.0 V. Cell 5 was cycled 5 times with the highest efficiency being 65%. Discharge currents were 1 mA or less. The internal cell resistances were as high as 6.8×10^3 ohms.

The results of this study led to cells with the following configurations for further work:¹⁴

1. $\text{Zn}/\text{AlCl}_3\text{--MEIC}(N=.33)//\text{Br}_2(13\% \text{ w/w in } N=0.42 \text{ MEIC,RVC/Pt}$

2. $\text{Cd}/\text{AlCl}_3\text{--MEIC}(N=.33)//\text{Br}_2(13\% \text{ w/w in } N=0.42 \text{ MEIC,RVC/Pt}$

NAFION was the separator in both cells and the internal cell resistances of 150--300 ohms were due primarily to the separators. The cadmium cell was reversible with an open-circuit potential of 2.0 V and was discharged to 70% of capacity with no apparent effect on rechargeability. The zinc electrode was not reversible.

Donahue examined metal-chlorine cells and metal-metal halide cells in basic and acidic melts. Metals used were aluminum, magnesium, and zinc and the halides were iron(III) chloride and copper(II) chloride. These cells contained no separator. The cathode compartment contained a saturated solution of the positive electrode material and was in direct contact with a binary melt of the same composition without the metal halide. RVC was used as the current collector in the cathode. Al/CuCl_2 primary cells gave an open circuit voltage of 2.1 V in basic electrolyte and were discharged at 1 mA. Secondary cells using acidic electrolyte gave an open circuit potential of 1.9 V and were discharged at 5 mA and charged at 2.5 mA. Discharge currents as high as 70 mA were mentioned, and discharge curves were presented for 10 mA.

More recently, Gifford and Palmisano¹⁵ constructed an Al/Cl_2 ,graphite cell that did not require an ionic separator. Their electrolyte was an acidic composition of 1,2-dimethyl-3-propylimidazolium chloride and aluminum chloride. Cells were cycled up to 100% depth of discharge over 150 cycles. Discharges were flat at about 1.7 V at currents of about 0.15 to 2.5 mA. The failing of this cell configuration is the low storage capacity of graphite for chlorine.

BATTERY PROBLEMS ASSOCIATED WITH BASIC AND ACIDIC MELTS

These earlier battery studies pointed out several problems with chloroaluminate electrolytes. Many of the problems were first pointed out by Donahue.¹² Solubility of positive materials in basic and acidic compositions mandate a separator. However, separators that have been used result in high internal cell resistances at room temperatures. As of this time no suitable ionic separator has been found for use in these electrolytes.

While the conductivities of these melts are reasonable, the viscosities are quite high, and there are strong interactions among the ionic species¹⁶ resulting in poor mass transport of reactants and products of battery reactions. As a result, cells using these electrolytes are not able to carry high currents, a detriment to obtaining high energy density. The viscosity and ionic interactions are decreased (thereby increasing conductivity) by adding nonaqueous solvents such as benzene, acetonitrile, or dichloromethane.¹⁷ The volatile solvents dilute the ionic species, add mass that does not contribute to the electrochemical reaction, and may not be acceptable for battery applications due to loss of these components through vaporization or excessive pressure if the battery were sealed.

RECENT STUDIES USING BASIC ELECTROLYTE WITHOUT A SEPARATOR

Recent attempts in this laboratory to build practical cells using chloroaluminate electrolytes without an ionic separator included the use of gas diffusion electrodes (GDE) as chlorine electrodes (similar to the concept proposed by Donahue of using an ion selective membrane with a chlorine electrode) and the use of less soluble compounds such as the sulfides of molybdenum and titanium as cathode materials.

All work was performed in a Vacuum Atmospheres drybox with a circulating helium atmosphere maintained at less than 15 ppm total oxygen and water content. Reagents

were used as received. Gas diffusion electrodes (AE-20 and AE-100) were obtained from Electromedia Corporation.

Basic melts were made by mixing weighted amounts of MEIC and AlCl_3 in the drybox. The basic melts were not treated to removed any protonic impurities.

Cell discharge/charge measurements were made using a PAR 173 equipped with a PAR 276 plug-in module controlled by a Zenith 248 personal computer running a program that has been described previously.¹⁸ Cells were charged and discharged at constant current to preselected cutoff voltages.

Cells with the configuration $\text{Cd}/\text{MEIC-AlCl}_3/\text{GDE}/\text{Cl}_2$ were constructed. Figure 2 shows an exploded diagram of the cell used. These cells gave an initial open circuit voltage of 2.1 volts, but the electrolyte apparently wetted the electrolyte side of the electrode, eventually coming in contact with and reacting with the metal current collector on the gas side of the electrode, imparting a blue-green color to the electrolyte. These cells delivered only 1 mA of current.

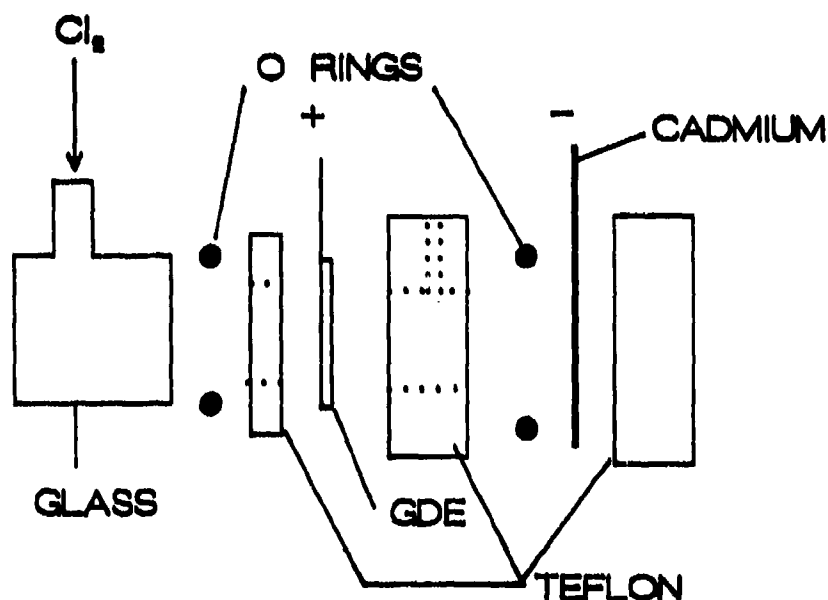


Figure 2. Exploded view of Cd/Cl_2 cell using a Gas Diffusion Electrode.

Another configuration used a flat cell similar to that described by Dymek *et. al.*¹⁴ The cell arrangement was $\text{Cd}/\text{N}=0.40, \text{CdCl}_2/\text{C}$ in which the cathode was a porous graphite sheet. These cells had an open circuit potential of 1.3 volts and were cycled between 0.5 and 2.2 volts at currents up to 1 mA. As with other chlorine/graphite cells, the capacity of this cell was unacceptably low.

Cells such as shown in Figure 3 were constructed with Cd anodes, MoS_2 cathodes, and basic electrolyte. Open circuit voltage was 1.1 – 1.2 volts and 2 mA could be drawn from the cell. A cellulose tube was used to contain the cathode but the MoS_2 proved soluble enough to self discharge and the cells delivered only a very small fraction of their theoretical capacity.

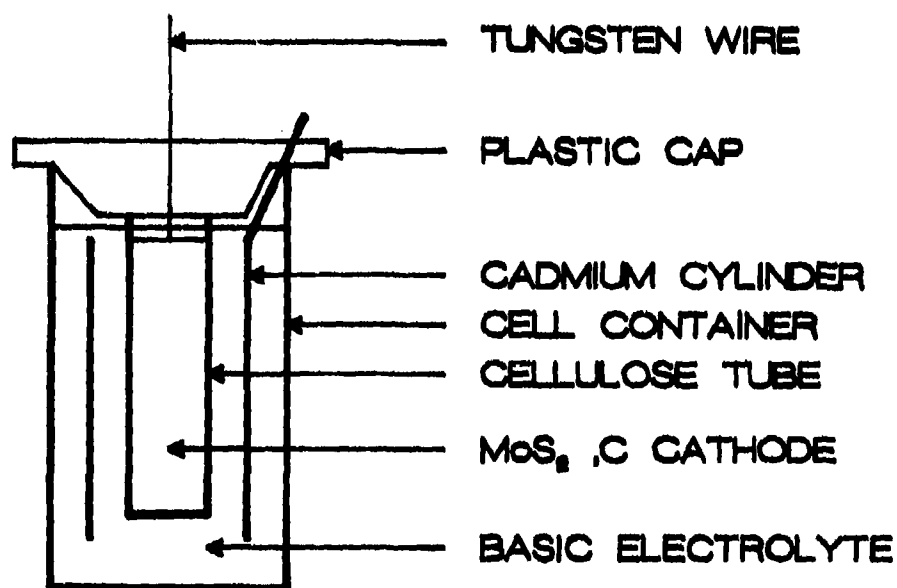


Figure 3. Cylindrical Cd/ MoS_2 cell.

CELL STUDIES USING BUFFERED NEUTRAL MELT

Recently the discovery was made that adding NaCl to an acidic melt resulted in a melt buffered to exactly neutral composition.¹⁹ By buffering the melt to neutral, the full electrochemical window of over 4 V becomes available, opening entirely new possibilities for battery applications. The increased electrochemical window makes the use of more active metals, such as sodium, potentially possible. Additionally, potential positive electrode materials such as the transition metal halides appear to be insoluble in the buffered melt, eliminating the need for an ionic separator.

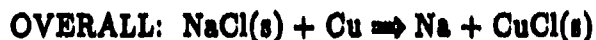
Experimental procedures were similar to those described in the previous section. Neutral electrolytes were made by first making a N = 0.55 melt and then removing protonic impurities by the addition of ethylaluminum dichloride.²⁰ These melts were then buffered by adding 10 percent excess of NaCl and stirring overnight. Electrochemical measurements were made using a PAR 273 Potentiostat. Battery discharges used the same equipment and procedures as described in the previous section.

In preliminary experiments copper electrodes were electrolyzed in buffered melt and scanning electron microscopy showed the formation of an adherent copper chloride layer on the surface of the copper metal.²¹ Chronoamperometry experiments showed that 100% of charge used to form the copper chloride was returned although cyclic voltammetry indicated the reaction was not classically reversible.²¹

Crude Na/CuCl cells were assembled in which sodium and copper were separated only by buffered melt or melt-saturated borosilicate glass mat. The expected cell reactions during charge would be sodium deposition from the buffered melt and by the formation of copper(I) chloride at the surface of the copper electrode.



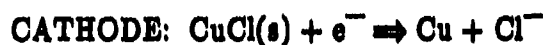
and, since melt is buffered:



For discharge, the expected reactions are:



and in buffered melt



and since melt is buffered:



The cells were much less than 50% efficient in charge recovery and repeated cycling resulted in rapid cell deterioration and failure. The first three cycles of such a cell are shown in Figure 4. Cell failure was attributed to irreversibility of the sodium electrode, probably due to the reduction of MEI^+ as evidenced by the appearance of a brown coating on the sodium surface.

While the first experiments showed a rechargeability problem with the sodium electrode, they did show some promise for primary cells. Primary cells of the configuration shown in Figure 5 were constructed using buffered chloroaluminate electrolyte. The anode

was a cast sodium rod with a tungsten wire current collector. The anode was made by pouring molten sodium metal into a teflon tube of appropriate diameter plugged at one end. When the sodium hardened, the teflon was cut away, exposing shiny but somewhat rough sodium metal. The cathode was a 50/50 weight percent mixture of CuCl_2 and graphite with a copper screen current collector. The anode and cathode were separated by a borosilicate glass tube containing electrolyte and a small amount of solid sodium chloride. The area of the sodium anode in contact with the electrolyte was about 4 cm^2 . Open circuit voltage of these cells was 2.75 volts at 25°C . The cells showed relatively low polarisation up to 3 mA, but above 3.2 mA the polarisation increased dramatically as shown in Figure 6. Internal resistance below 3 mA was less than 70 ohms. Cells were discharged at currents up to 3 mA.

Na/CuCl Secondary Cycles 1 - 3

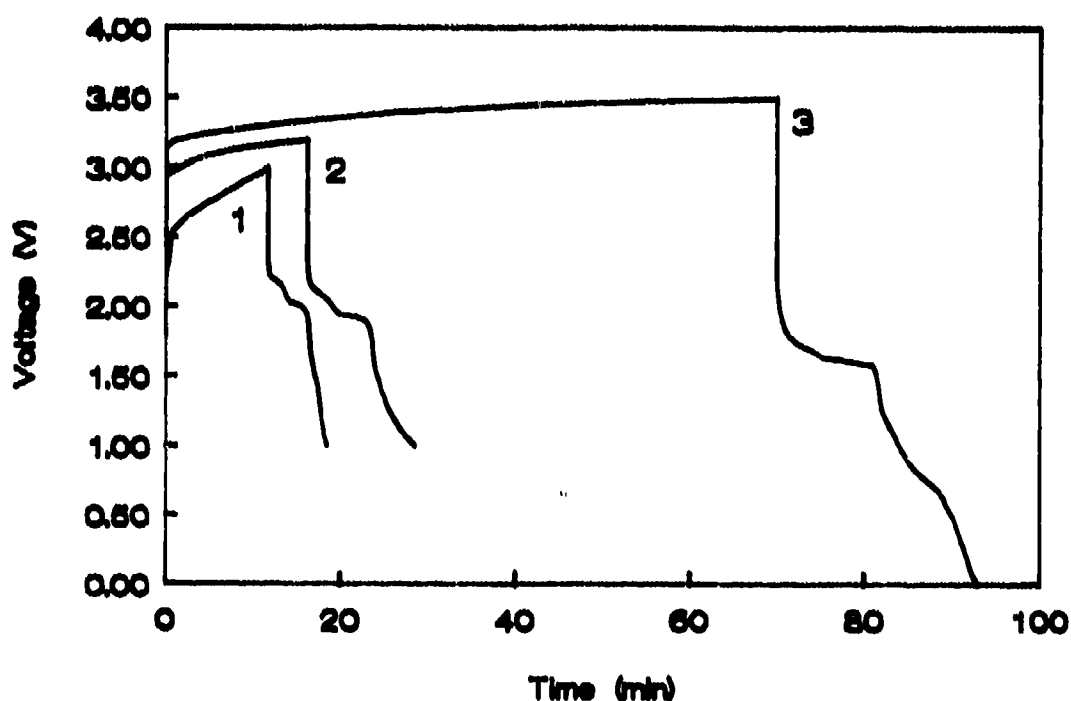


Figure 4. First three cycles of a crude Na/Cu cell. Cycle 1: 1 mA, 3.0 V charge cut-off. Cycle 2: 0.5 mA, 3.2 V charge cut-off. Cycle 3: 0.5 mA, 3.5 V charge cut-off.

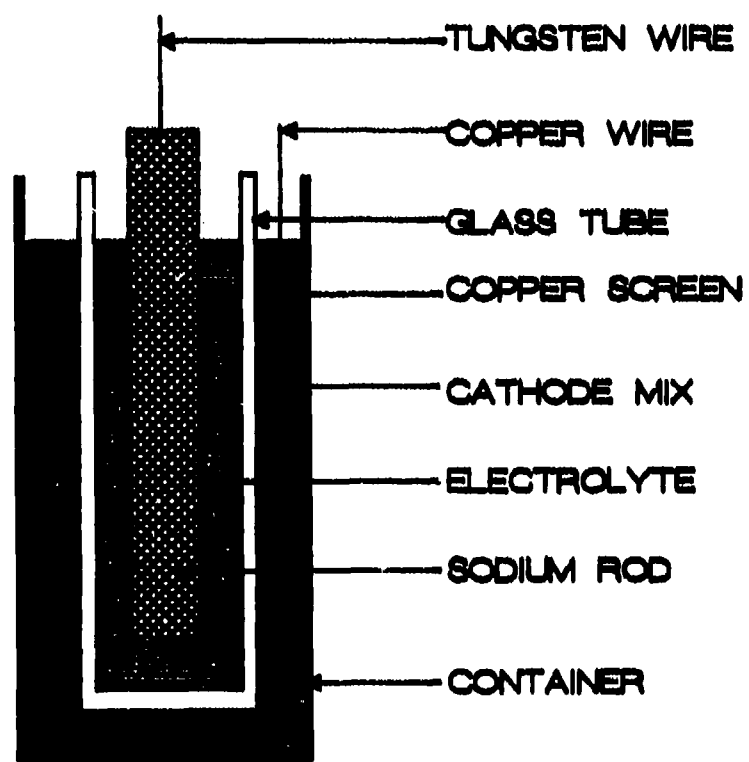


Figure 5. Na/CuCl₂ primary cell design.

Na/CuCl₂ CELL POLARIZATION

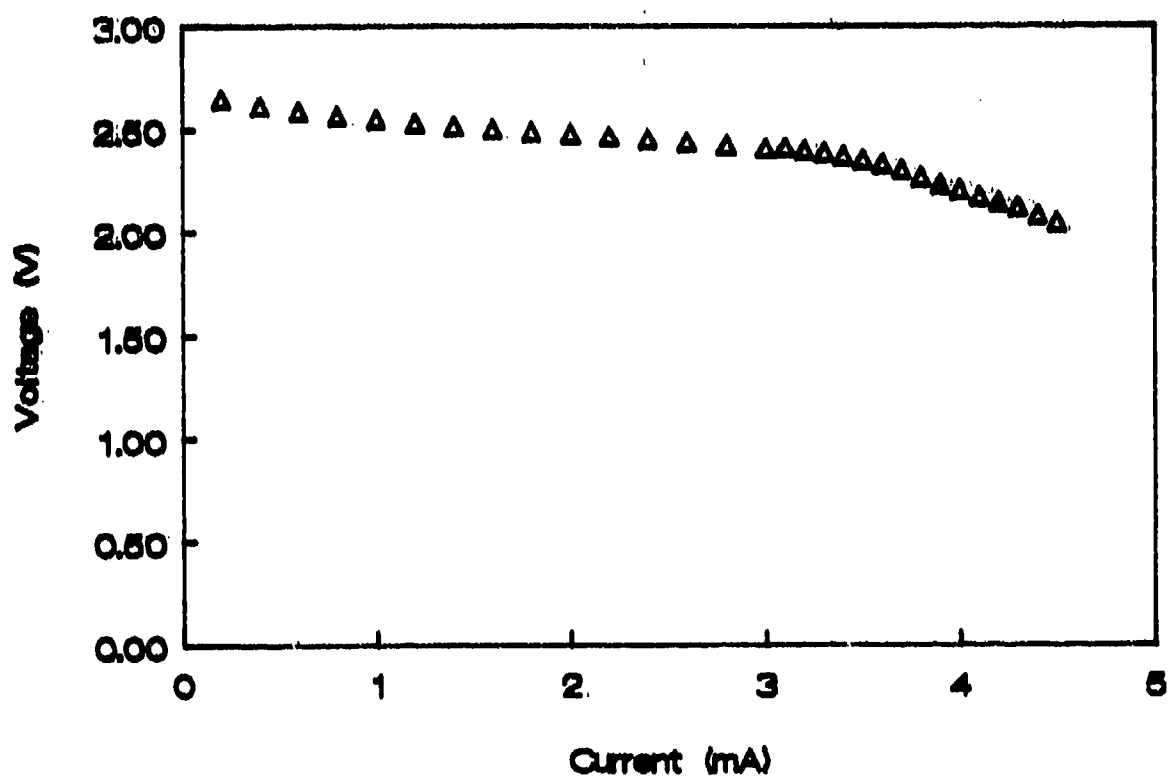


Figure 6. Polarisation of Na/CuCl₂ cells containing buffered neutral chloroaluminate molten salt electrolyte.

Discharge experiments were inconsistent. Early experiments, Figure 7, showed high voltages for relatively long times after an initial voltage delay. The discharge to 1.0 V represented only about 11 percent of the theoretical capacity of the cathode. These early discharges seemed to indicate a dependency on the time the cell was on open circuit stand prior to the discharge. Other tests were made that varied the open circuit stand from 0 to 70 hours. All subsequent tests failed to maintain the high voltage regardless of length of open circuit stand. At the same time the effect of the solid sodium chloride in the anode compartment was examined by discharging cells that did not contain added NaCl. The results shown in Figure 8 indicated no significant difference on these factors. All the curves are similar, with erratic voltages, especially near end of life, that are predominantly near 1.50 volts and an abrupt voltage drop at the end of discharge. Again, in all cases the delivered capacity was much lower than theoretical.

Examination of cells after discharge showed the formation of a heavy black coating on the sodium anode. The electrolyte remained clear and showed no evidence of copper chloride dissolution. The layer formed on the sodium electrode seems to be responsible for the observed discharge behavior. When the circuit was opened, the voltage immediately jumped from 1.0 volt to over 2 volts where it remained. When the anode was removed, the layer scraped off, and replaced in the cell, it was discharged again at the same current. The erratic discharge curves can be attributed to the changes in the surface of the anode due to the formation of the passivating layer.

In order to examine the cause of the passivating layer, electrolyte components and preparation were varied for some cell tests. The usual method of melt preparation involves the addition of ethylaluminum dichloride to remove protons. Cells using electrolyte that was not treated with EtAlCl_2 were compared to cells using electrolyte deprotonated in the usual way. No significant differences were observed (See Figure 9).

To examine the possibility that the layer is the result of a reaction between sodium

and some component of the electrolyte or an impurity left as a result of the synthesis of the MEIC, electrolyte was prepared from MEIC recrystallised from diethyl ether instead of the usual acetonitrile. Cells using the new electrolyte showed considerably improved discharge performance. Figure 10 compares the discharge for a cell using electrolyte made from MEIC recrystallised from diethyl ether to a cell made from the MEIC prepared in the original way. Cells made with the new electrolyte showed higher voltage for a much longer time and the discharge curves were smooth and more reproducible. Cells with the new electrolyte discharged over 50% of theoretical capacity to 1.0 volt. The anode was still covered with a black deposit which may remain the reason for the abrupt voltage decrease at the end of discharge.

The surface of the electrode was examined by scanning electron microscopy/EDAX. No significant surface features were observed. Two samples were used. Sample 1 came from an electrode used in a cell containing electrolyte prepared in the original way. This same was stored in a closed bottle in the drybox antechamber for 6 days before analysis. Sample two was from a cell using the new electrolyte and was analysed very shortly after taken from the cell. The elemental composition of both samples showed aluminum, chlorine, and some sodium. Sample 1 also contained oxygen. Neither sample had carbon present on the surface. The lack of carbon indicates that the layer is not caused by the chemical reduction of MEI^+ by sodium, but the reaction at the anode apparently involves some oxidation of the tetrachloroaluminate anion. The reaction of Na^+ formed during discharge with AlCl_4^- forming an insoluble product was considered unlikely since NaAlCl_4 has been added to MEIC melts and no insolubilities were observed.¹⁶

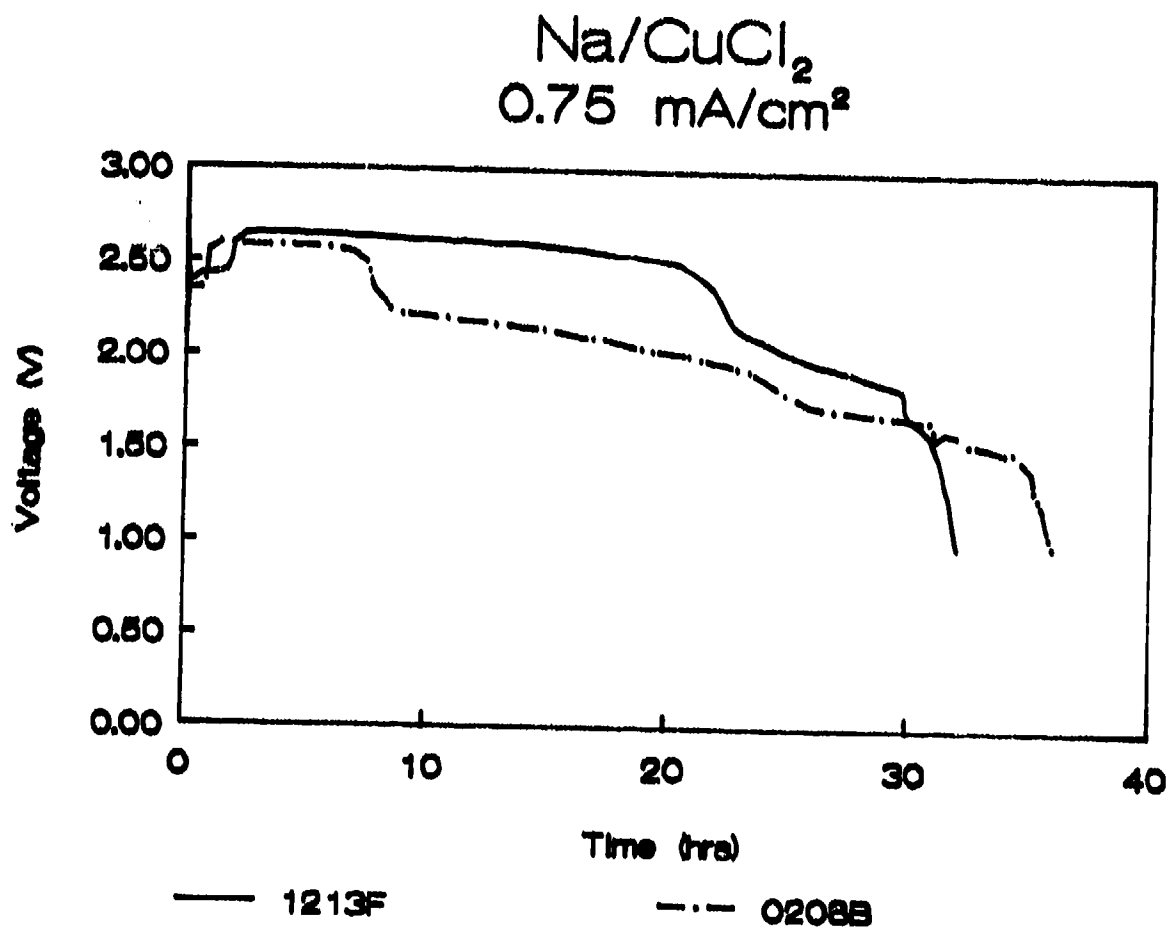


Figure 7. Discharge curve for Na/CuCl_2 cell. Electrolyte is buffered neutral aluminum chloride-1-methyl-3-ethylimidazolium chloride with solid NaCl added to the anode compartment. Test 1213F included a 24 hour open circuit stand while test 0208B was on open circuit for 5 hours prior to discharge.

Na/CuCl₂
0.75 mA/cm²

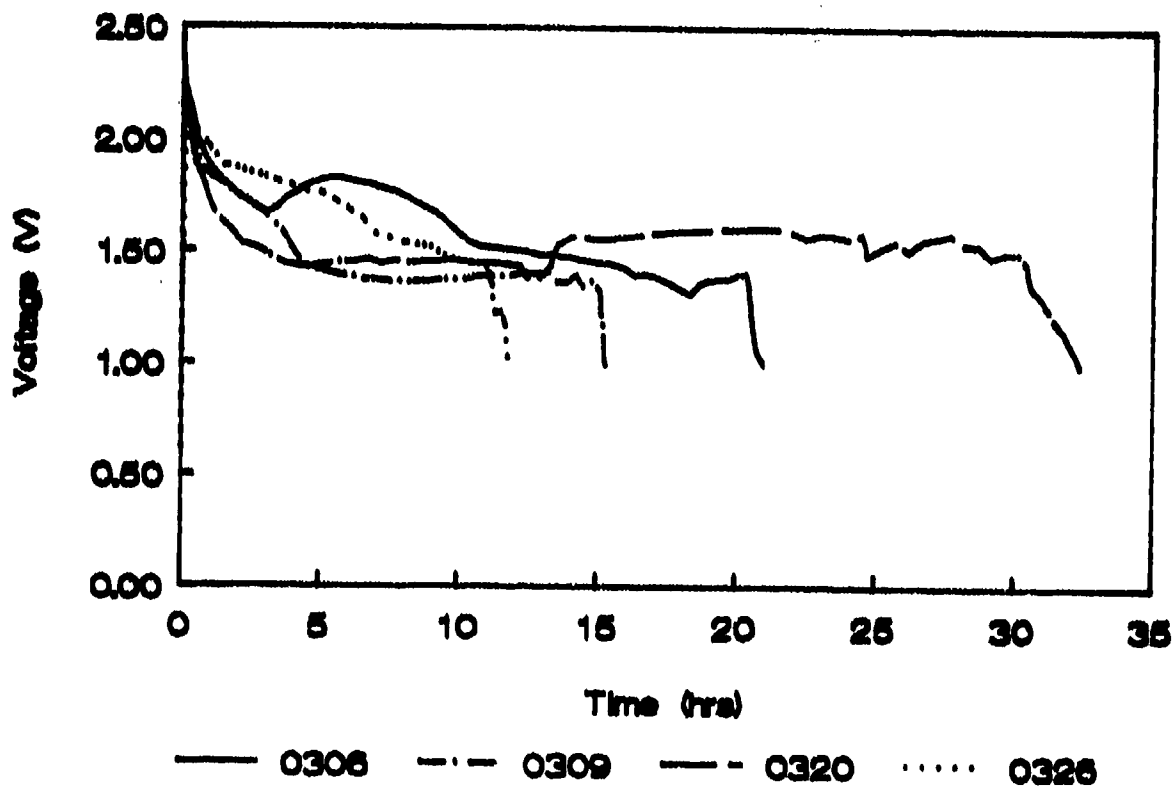


Figure 8. Discharge curves for cells showing the effects of different open circuit stands and addition of solid sodium chloride to the anode compartment. Tests 0306 and 0309 contained no solid sodium chloride in the anode compartment. Tests 0306 and 0320 had no open circuit stand prior to discharge. Test 0309 was on open circuit for 18 hours and 0326 was on open circuit for 72 hours.

Na/CuCl₂
0.75 mA/cm²

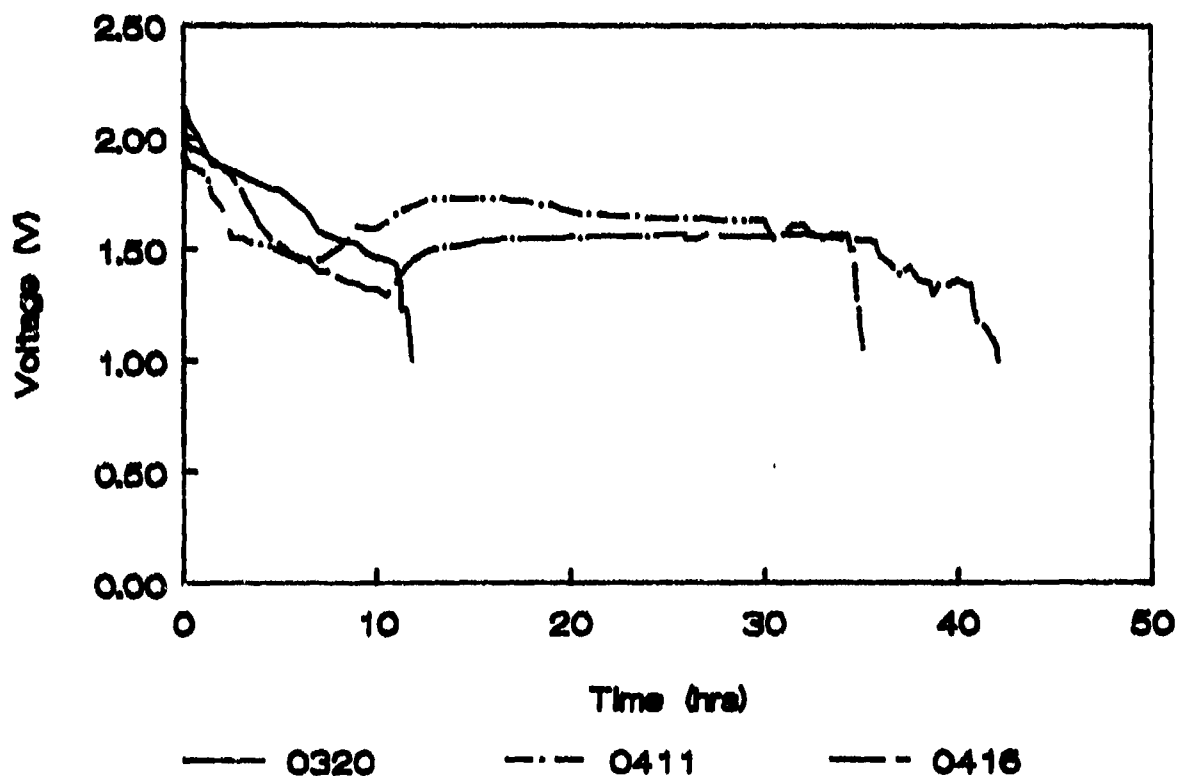


Figure 9. Discharge comparison for cells in which the electrolyte was deprotonated with ethylaluminum dichloride. In test 0320 the electrolyte was deprotonated by usual addition of ethylaluminum dichloride. Tests 0411 and 0416 used electrolyte that was not deprotonated. All cells contained solid NaCl in the anode compartment. Tests 0320 and 0411 had no open circuit stand.

Na/CuCl₂
0.75 mA/cm²

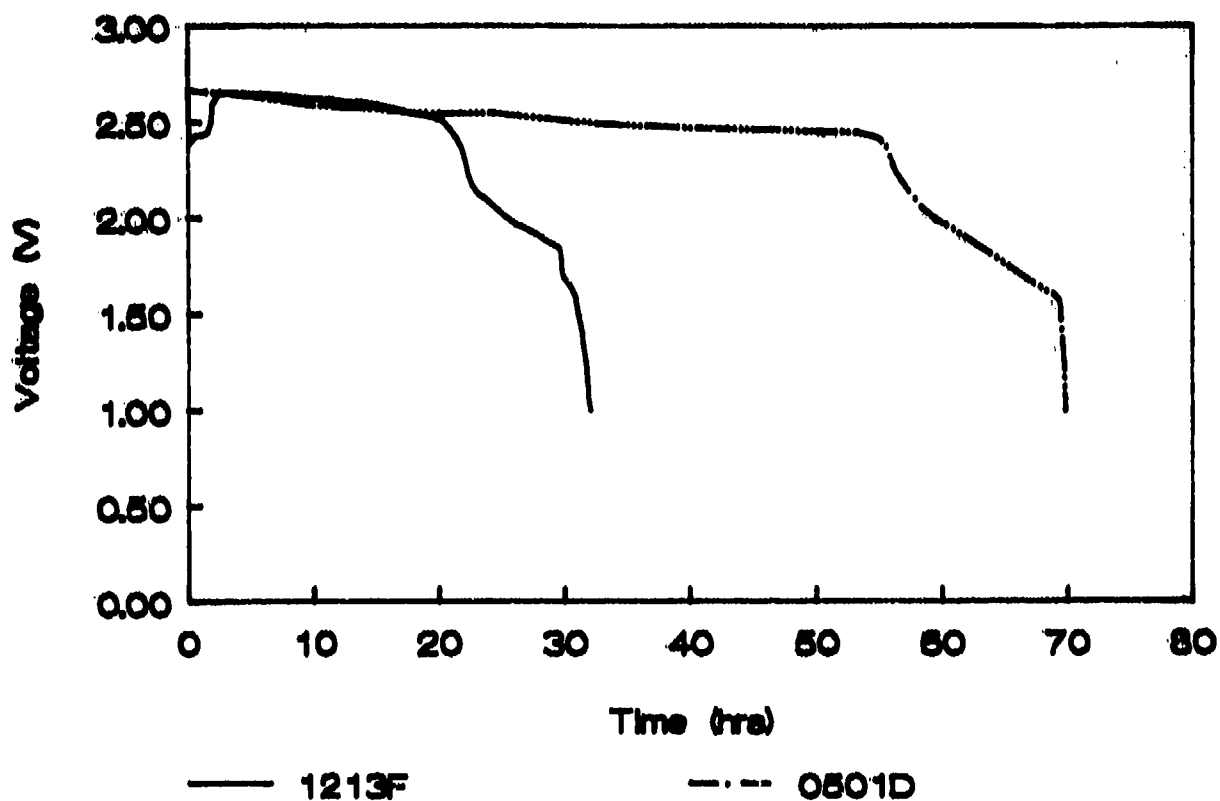


Figure 10. Comparison of cells using electrolytes made from MEIC prepared using acetonitrile versus diethyl ether. Test 1213F used electrolyte made using the original preparation method. Test 0501D used MEIC made using diethyl ether.

CONCLUSIONS

The discovery of a way to buffer the room-temperature chloroaluminate melts to the neutral composition has eliminated at least one major obstacle to the goal of a practical battery using chloroaluminate electrolytes. Prospective positive electrode materials appear to be insoluble in the buffered melt which eliminates the need for an ionic separator. However, this same insolubility may pose another problem in the form of a nonconductive reaction product adhering to the surface of the sodium electrode. Test cells have shown that Na/CuCl₂ primary cells can be discharged at 2.5 volts and near 1 mA/cm² for more than 50 percent of capacity.

The physical properties of the melt may prove to be the limiting factor in any room-temperature high energy density cell. The conductivity and viscosity of these melts do not favor the delivery of high current. While Donahue has alluded to currents as high as 70 mA(12), other cell studies using room-temperature chloroaluminates, including this one, have reported currents in the range of 1 to 3 mA.

While the discovery of buffered chloroaluminates has advanced the realization of a practical high voltage battery using these electrolytes, the prospects for a room-temperature chloroaluminate battery with high energy density have not improved.

RECOMMENDATIONS FOR FUTURE STUDIES

Measure conductivity and other properties of buffered melt:

While the buffered melt is considered neutral in composition, its properties are not necessarily identical to the neutral unbuffered composition. The ionic interactions need to be examined in the same way as was done for the unbuffered melts. The conductivity of the buffered melts needs to be measured as a function of temperature and amount of excess sodium chloride. Other physical properties such as viscosity and density should also be characterized.

Detailed study of sodium in buffered melts:

More information must be obtained about the behavior of sodium in these melts. While sodium deposition has been reported from buffered melts,²² cell tests here have not demonstrated the deposition on a sodium substrate. Discharge of primary cells resulted in the formation of a nonconductive layer on the surface of the sodium. The nature of this layer needs to be investigated further. A way needs to be found to eliminate this layer or to make it conductive. Possible solutions to study are alloying metals or electrolyte additives.

Other buffering agents:

Other metal chlorides such as KCl, MgCl₂, or CaCl₂ may also buffer the chloroaluminate melts. Melts buffered by MgCl₂ for example may show favorable battery behavior with magnesium as the negative electrode material.

Alternative positive electrodes:

Other transition metal halides and sulfides need to be examined as possible cathode materials. Possibilities include iron(III) and molybdenum(VI) chlorides as well as the sulfides of iron, molybdenum, and titanium. The methods of fabrication of cathodes can be improved. For example, if the positive electrode material can be immobilized in a fixed matrix such as polytetrafluorethylene (PTFE) the glass fiber tube can be eliminated.

Elimination of the physical barrier between anode and cathode should reduce the internal resistance even further and allow higher currents.

Dymek has indicated that the compound MEICl_2 may be a way to efficiently store chlorine for use in chlorine cells.¹³ This compound could be used in the same configuration as the Na/CuCl_2 cells reported here with MEICl_2 replacing CuCl_2 . If the problems with the sodium electrode are solved, and the sodium electrode combined with a good chlorine storage source, the result would be a cell having exceptional energy density and voltage. The Na/Cl_2 couple has a theoretical energy density of 1833 Wh/kg.¹³

A similar approach would be to use a basic melt saturated with bromine as the cathode. Dymek *et. al.*¹⁴ has shown that in basic melt, bromine reacts with the free chloride to form Br_2Cl^- anion. Either MEICl_2 or Br_2Cl^- would give higher energy densities and voltages than the transition metal halides.

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